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EXPERIENCE WITH COPPER OXIDE PRODUCTION IN ANTIPROTON SOURCE COMPONENTS AT FERMI NATIONAL ACCELERATOR LABORATORY

Christine R. Ader
Fermi National Accelerator Laboratory
MS-340, P.O. Box 500
Batavia, Illinois 60510
630-840-6342
Fax: 630-840-2677
E-mail: cader@fnal.gov

Elvin R. Harms, Jr.
MS-341
630-840-4387
Fax: 630-840-8737
E-mail: harms@fnal.gov

James P. Morgan
MS-341
630-840-5236
Fax: 630-840-8737
E-mail: jpmorgan@fnal.gov

ABSTRACT

The Antiproton (Pbar) Source at Fermi National Accelerator Laboratory is a facility comprised of a target station, two rings called the Debuncher and Accumulator and the transport lines between those rings and the remainder of the particle accelerator complex. Water is by far the most common medium for carrying excess heat away from components, primarily electromagnets, in this facility. The largest of the water systems found in Pbar is the 95 degree Fahrenheit Low Conductivity Water (LCW) system. LCW is water which has had free ions removed, increasing its resistance to electrical current. This water circuit is used to cool magnets, power supplies, and stochastic cooling components and typically has a resistivity of 11-18 megaohms-cm.

For more than ten years the Antiproton rings were plagued with overheating magnets due to plugged water-cooling channels. Various repairs have been tried over the years with no permanent success. Throughout all of this time, water samples have indicated copper oxide, CuO, as the source of the contamination. Matters came to a head in early 1997 following a major underground LCW leak between the Central Utilities Building and the Antiproton Rings enclosures. Over a span of several weeks following system turn-on, some twenty magnets overheated leading to unreliable Pbar source operation. Although it was known that oxygen in the system reacts with the copper tubing to form CuO, work to remedy this problem was not undertaken until this time period. Leaks, large quantities of make-up water, infrequent filter replacement, and thermal cycling also result in an increase in the corrosion product release rate.

A three-pronged approach has been implemented to minimize the amount of copper oxide available to plug the magnets:

- Installation of an oxygen removal system capable of achieving dissolved oxygen concentrations in the parts per billion (ppb) range.
- Regular closed-loop filter/flushing of the copper headers and magnets and stainless steel header during down periods.
- Installation of a full-flow filtration system designed to remove any CuO produced by the trace amounts of dissolved oxygen in the LCW system.

All three items have been completed. The dissolved oxygen concentration is now routinely on the order of 15 ppb and returns to that level within 8-12 hours following an upset condition such as a leak. Prior to installation of the oxygen removal system, oxygen levels were approximately 3000 ppb. Particle analysis of the water before-and-after filter and flushing of the LCW system indicates a cleaner system. Another round of filter/flushing occurred shortly before the scheduled start-up and will be performed during down periods when deemed necessary by newly-installed instrumentation.

The full-flow filtration system has been recently commissioned. The system consists of two parallel filter housings, with a rated total flow capacity of 2500 gpm at 300 psi, piping to the LCW supply header and associated instrumentation.

INTRODUCTION

The Pbar cooling water system is a 95 degree Fahrenheit closed-loop that recirculates high purity water. The water circulates from the Central Utilities Building (CUB) to the Pbar electromagnets and back to CUB. An overall view of the facility is shown in Figure 1. The system consists of approximately 2000 feet of ten-inch stainless steel pipe and 2000 feet of four-inch stainless steel pipe. In the tunnel, the stainless-steel headers distribute LCW to a total of 21 two-inch copper headers from which the magnets are fed in parallel.

The LCW in the loop typically has a resistivity of 11 to 18 megaohms-cm. The sidestream-polishing loop that includes a mixed bed ion exchanger has a resistivity of 16 to 18 megaohms-cm. This loop polishes 15 gallons per minute, which represents about one percent of the 1600 gpm recirculation rate. The system volume is about 13,000 gallons, which is polished every 16 hours and has a typical resistivity of 9 to 11 megaohms-cm.

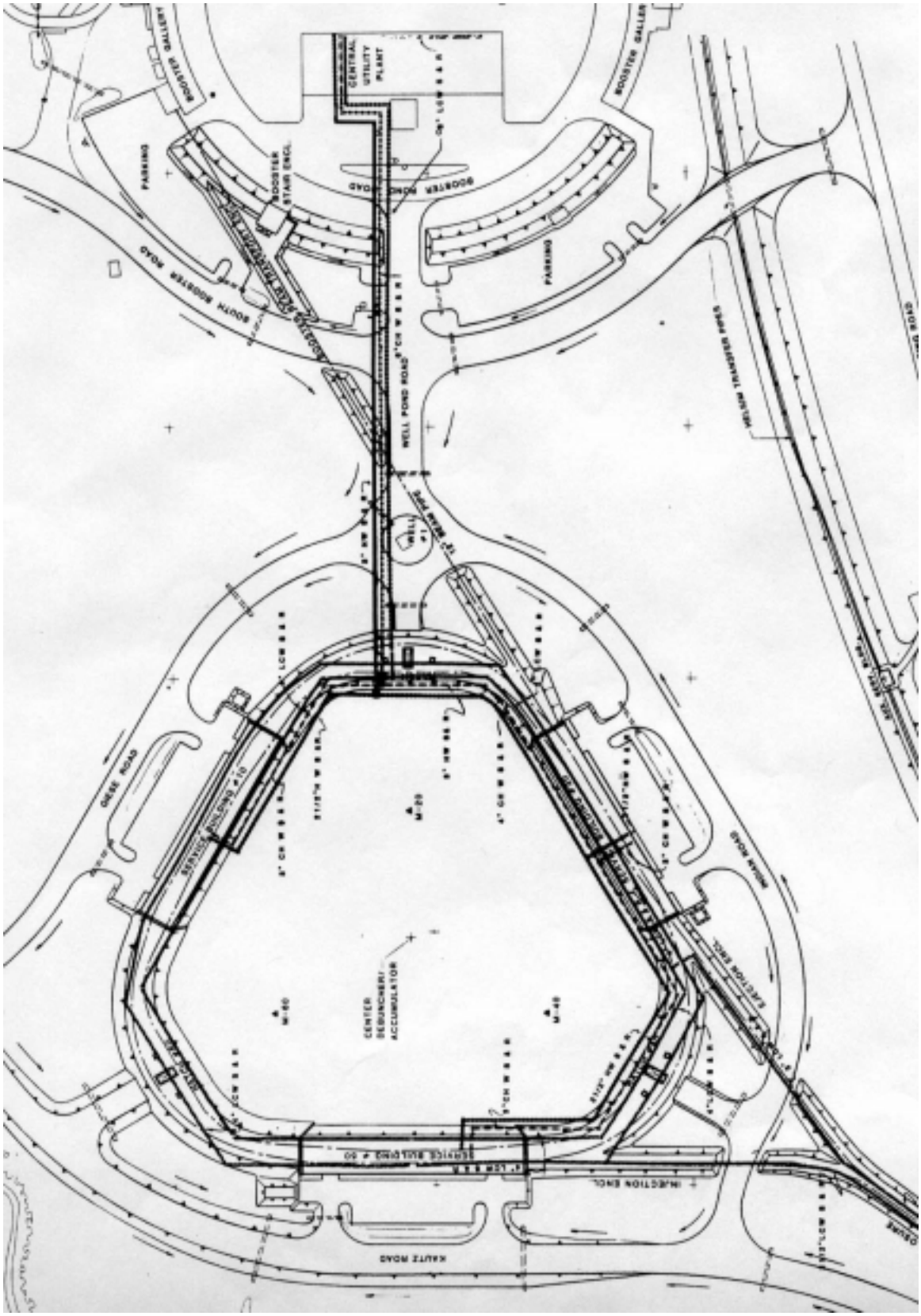

Figure 1. General Layout of the Antiproton Source Layout

One of the components cooled by this system is the small quadrupole (SQ) type magnet. These magnets serve as the lens for the antiproton beam. Many of these magnets have had problems with plugging by CuO. As early as eight to nine months after initial operation in 1985, the magnet LCW flow-controlling began to plug with copper oxide leading to overheating magnets, hampering normal operation (Meisner, 1999). A typical quadrupole contains four parallel cooling loops made up of 0.1875" diameter copper channel tubing, with 132 turns (each turn is twice the magnet length), 18 to 51.6 inches in length, with a water flow rate of 0.33 to 0.51 gpm per magnet. The iron mass temperature is normally elevated 10-20 °F when electrical current is flowing through the coils while the temperature of an overheating magnet can be elevated as much as 70 °F.

Pbar magnet iron temperature for Collider Run 1b, from 11/93-2/96 is shown in Figure 2. Up to 20 magnets during one-week periods were found to overheat. The sample periods varied depending on the run schedule. Additionally, Figure 3 shows the number of overheating magnets following the major underground LCW leak between the Central Utilities Building and the Antiproton Rings enclosure in early 1997. The numbers in parentheses are the number of magnets that were flushed during the selected time period. Thermal cut-off switches, klixons, have been installed on many of the components in order to shut them off if they overheat.

COPPER OXIDE PRODUCTION - THEORY AND EXPERIENCE

Copper and copper alloys are often used for water cooling systems because they are relatively inexpensive, easy to machine, tend to be non-fouling (due to their smooth surface), have high heat transfer capability compared to many materials, and have excellent corrosion resistance in most cooling applications. In accelerators, magnet cooling channels also carry electrical current and therefore, need to have low resistance. Some of their drawbacks include vulnerability to ammonia and chelants and susceptibility to erosion. Depending on the particular material, gas concentration, water chemistry, temperature, and flow velocity, the corrosion mechanisms include oxidation, exfoliation, crevice corrosion, and erosion-corrosion. These mechanisms have been investigated for several decades.

The dissolved oxygen and carbon dioxide in the LCW causes corrosion of copper and copper alloys by converting metallic copper to copper oxide. The copper wall of the piping will form a protective oxide layer using the oxygen available in the water. The bare metal wall is then available to form additional oxides. The process, called passivation, will continue as long as the conditions remain constant.

During upset thermal, hydraulic (flow or pressure), or mechanical conditions the copper oxide can be induced to slough off by thermal cycling or by other upset conditions. Any chemical reaction speed goes up with temperature (~exp(-A/RT)) where A is the activation energy, R is the gas constant, and T is the temperature. Although the solubility of gases in water decreases with temperature, the first effect dominates (Scholer and Euteneuer, 1988, p. 1068).

Stator cooling systems in power generation equipment have low conductivity water (3-10 megohms-cm) and have had problems with copper oxide plugging with their copper cooling windings with openings as small as 1.5 mm x 5 mm (Moliere, Verdier, and Leymonie, 1990, p. 183).

Oxygen levels should either be kept at saturation (at atmospheric pressure, deionized water is saturated at about 3400 ppb oxygen at 170° F) to develop and maintain a passivated surface or at levels less that 30-50 ppb to prevent corrosion. Corrosion is actually maximized when the value is around 200-300 ppb. Corrosion rates were found to be seven times lower than the maximum rate when oxygen was maintained at very low levels (about 10 ppb) or at high levels which is about four ppm. (Kang, et. al, 1994 and Himmelblau, 1960).

However, one of their studies had problems with cooling water blockage even with oxygen levels around 20 ppb. They found that using one μm filters suppressed the problem (they had previously used up to five μm filters). Another one of their studies found filters at one μm with 98% efficiency to be helpful in preventing copper oxide plugging. Copper oxide was found on their filters even with oxygen levels less than five ppb (Kang, et. al, 1994 and Himmelblau, 1960).

Additionally, if the oxygen level suddenly increases from a low level to a higher level (i.e., <20 ppb to 2000 ppb), a large increase in the release of suspended copper oxide corrosion particles occurs. This release can deposit throughout the cooling system, leading to a reduction in heat transfer and other deposition-related problems. This occurred in their systems because of leaks, large quantities of make-up water, or from too frequent cleaning of their filters. They also found that thermal cycling resulted in an increase in the corrosion product release rate (Moliere, Verdier, and Leymonie, 1990, p. 183).

Water samples from the Pbar LCW system were submitted for particle size analysis and indicated that the median-sized particle is between 0.55 to 0.60 μm and that the majority of the particles are smaller than five μm.

Additionally, at the Deutsches Elektronen-Synchrotron (DESY) laboratory in Hamburg, Germany, which conducts high-energy and particle physics research, it was found that the copper depletion in the LINAC II accelerator was very small without oxygen present. They predicted that about 95 kg would be lost after 25 years of operation using a system with oxygen. This would be equivalent to 2.8% of the cooling pipes with a total weight of 3350 kg. With deionized water, oxygen and carbon dioxide produce about 91% of the solvent copper ions. The LINAC II would have lost about 8.5 kg. of copper over 25 years using a closed system without oxygen (Poggensee, 1993). Up to 50 micron/year can be removed from the pipe walls due to oxygen and carbon dioxide. This means that after 20 years, one mm of the pipe wall could be removed.

Corrosion does not occur evenly in the system (Schoeler and Euteneur, 1988) and progresses much slower in straight sections than in bends or reducing sections. In the LINAC II at DESY, damage due to corrosion was found at several bends after three years of operation while the long straight sections do not show any corrosion even after 25 years (Poggensee, 1993). This may be due to the fact that laminar flow in straight sections may reduce the rate due to oxygen depletion near the surfaces. Additionally, if the copper ion concentration is near saturation, a rise in temperature favors the formation of CuO deposits (by lowering the concentration of hydrogen ions) and therefore the obstruction of narrow cooling channels, especially at low-water flow velocities (Scholer and Euteneur, 1988, p. 1068).

In Pbar, a preferential deposition of copper (mainly as CuO, tenurite) at the inlet of the elbows to the quadrupole magnets is probably related to the sharp drop in the velocity of the water in this region.

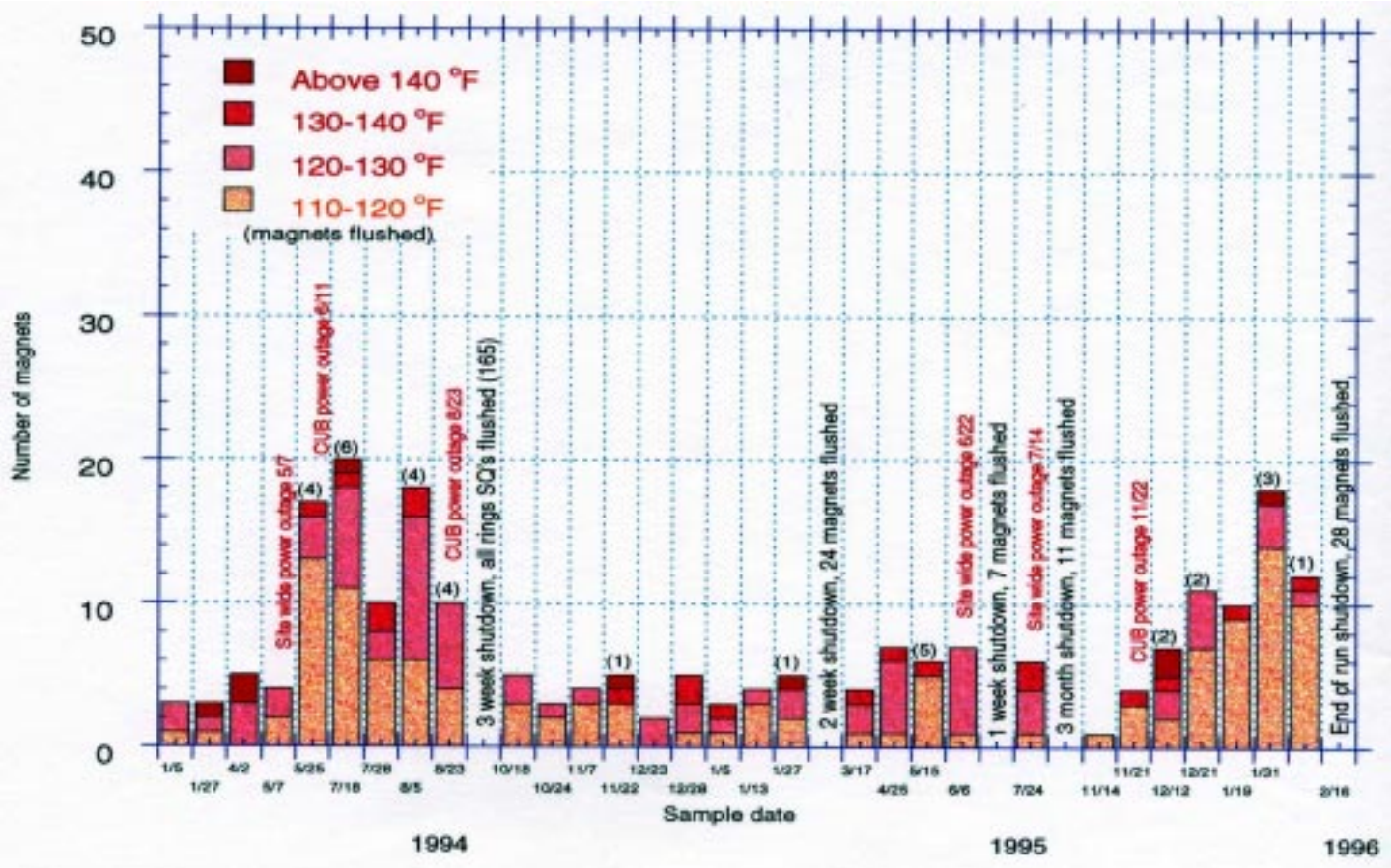

Figure 2. Pbar Magnet Iron Temperature, Collider Run 1b (11/93-2/96)

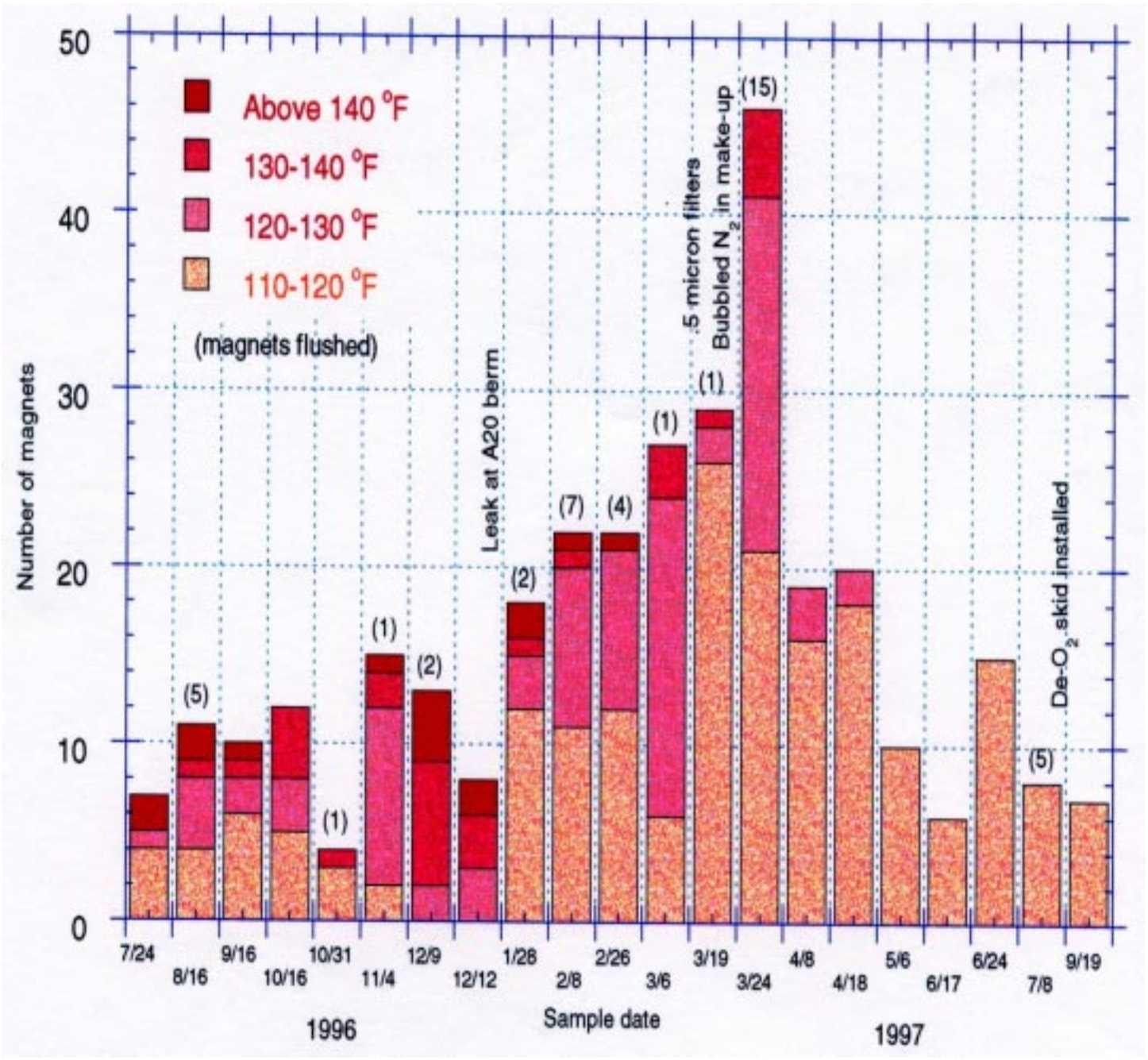

Figure 3. Pbar Magnet Iron Temperature, Fixed Target Run (1996-7)

Because Pbar initially had an oxygenated system, a copper oxide film formed on the copper piping. Typically, on cleaned copper, water containing oxygen at two parts per million or greater promotes passivation of copper surfaces in about 10 days by producing an adherent, black, copper oxide film (Moliere, Verdier, and Leymonie, 1990, p. 183). Cuprous oxide (Cu_2O) is essentially the protective layer adjacent to the metal surface. The outer cupric oxide, CuO (or $Cu(OH)_2$), is formed by oxidation of the cuprous ions. Formation of the cuprous oxide is preferred at lower reducing potentials, whereas with higher potentials (oxidizing) the growth is predominantly CuO. Oxygen is an oxidizing substance, so it will directly affect the oxidation/reduction potential levels in the system water. Control points of the oxygen concentration vary among different water chemistry treatments, but can typically be summed up in two methods. The first method attempts to remove as much oxygen as possible (typically down to five parts per billion or lower) through some form of mechanical and/or chemical means (Dooley, 1996, p. 360). The second method maintains a higher level of oxygen, typically 50 to 200 ppb (Filer, 1998, p. 55).

Since low oxygen is now maintained in the system, passivation is less likely to occur which can lead to the release of particulate corrosion products that can deposit throughout the system. Copper hydroxide [Cu(OH)2] can form at very low levels of oxygen and is half as dense as copper oxide. This species can create problems similar to copper oxide.

POTENTIAL SOLUTIONS

Closed systems reduce corrosion problems drastically because the recirculating water is not continuously saturated with oxygen, as in an open system. The only possible points of oxygen entry are at the surface of the reservoir tank and leaks. With the small amount of makeup water required in an closed system, adequate treatment can all but eliminate corrosion and accumulations of corrosion products.

Some of the techniques that have been used to reduce the copper corrosion in Pbar have been to regenerate the ion exchange columns with sodium sulfate and by maintaining a nitrogen blanket on the make-up/expansion tank. The nitrogen blanketing of the makeup tank eliminates most of the oxygen entering the system and this was done starting in March of 1997.

Oxygen scavengers are organic and/or nitrogen-containing chemicals such as hydrazine that consume oxygen via an oxidation-reduction reaction. However, the addition of hydrazine has had a detrimental effect in some plants since removing oxygen by scavengers will lead to a strongly reducing environment (-300 mV or lower), which has actually been seen to increase the erosion/corrosion of iron-based materials as well as the flow-accelerated corrosion (Filer, 1998, pp. 60-61). They are often used in electric utility plants to scavenge the traces of dissolved oxygen that remains following vacuum deaeration. Vacuum deaerators were considered for this application but were ruled out because of their cost and size.

Another chemical that reduces copper corrosion, benzotriazole, is chemically adsorbed onto the copper and copper-alloy surfaces and forms a stable, inert film that affords long-term protection. This copper-benzotriazole film reinforces the existing oxide film, thus reducing corrosion. In LCW systems, the largest drawback for these corrosion inhibitors is that they change the conductivity of the water. In Pbar, the conductivity is vigorously regulated and benzotriazole can alter the conductivity up to 10 percent using amounts that would be effective at decreasing copper corrosion (Walker, July 1973). The power supplies cooled by LCW are regulated to one part per million. The magnitude of this change of conductivity would cause the power supplies to exceed this level of control. Additionally, these chemicals will deteriorate with radiation (Poggensee, 1993).

The Electric Power Research Institute (EPRI) philosophy is to keep the cycle chemistry simple and minimize chemical additions such as alkalizing and/or oxygen scavengers to feedwater systems (Dooley, 1996, p. 359). Pbar has followed this philosophy. Therefore, these types of chemicals have not been used in the Pbar LCW.

The solution ultimately arrived at was to not affect the water chemistry (conductivity issues), but rather take a generally passive approach to minimize the amount of CuO produced, and remove the small amounts that are generated before it can lodge in the accelerator components. This approach also has the advantage of being less labor-intensive and in the long-term less expensive. Therefore, a three-pronged approach was implemented which includes an oxygen-removal skid, flushing, and a full-flow filtration system. Additionally, flow through the entire system is maintained even during extended maintenance periods.

PROBLEM-SOLVING APPROACHES

Oxygen-Removal Skid

An oxygen removal system was brought on-line in July 1997. This system has skid-mounted membrane contactors that transfer dissolved gases from the aqueous stream.

This system was designed by Culligan to Fermilab's specifications to handle 40 GPM from the main 2,000 GPM loop and can reduce the dissolved oxygen content from near saturation level to less than 10 ppb in a single pass. This is done by modulating the flow of sweep nitrogen gas along with the use of vacuum.

The system has nine 4" X 28" hydrophobic membranes, manufactured by Hoechst-Celanese, arranged in a 1:1:1 array configuration with three parallel arrays. In the normal operating mode of the system, two of the three arrays are used.

Each membrane consists of hydrophobic polypropylene micro-porous hollow fibers. The fibers have small pores in their walls to allow dissolved gases to pass through but not liquid water. The design is analogous to a shell-and-tube heat exchanger. The water stream passes on the outside of the fibers (shell-side), while a vacuum and a sweeping gas such as nitrogen are applied to the tube-side of the hollow fibers. The sweeping gas pressure must be below that of the water. The difference in the partial pressure of oxygen between the tube and shell sides provides the driving force for gas removal. The large surface area of the material permits the system to reach equilibrium very quickly, which rapidly removes the oxygen from solution (D'Angelo, 1995, p. 61).

The contactors, piping, instrumentation including dissolved oxygen monitors, vacuum pumps, and control panel are mounted on a relatively compact skid measuring 120" x 80" x 77" high. Flexibility was designed into the system so that in the case of a significant system upset, make-up water can be deoxygenated before entering the main stream. Water from different sources can also be deoxygenated simultaneously by manually configuring the valving to the contactor arrays.

Flushing

Pbar started flushing/filtering the individual small quadrupoles in the summer of 1993. Two flushing skids that use cartridge filters and a turbidimeter, which detects the amount of particles in the water, are now used to backflush each magnet while the copper manifolds are filtered.

The United States Navy has implemented a cleaning procedure for their power amplifiers used in most of their very low frequency transmitters. These transmitters dissipate such high power that they must be cooled by water continuously flowing at high velocities through narrow channels located at the outer surface of the anode. Their cleaning solution consists of 1.5% citric acid, 1.75% dibasic ammonium citrate, and 1% to 2% erythorbic acid (Ervin, 1990).

Pbar used a proprietary de-liming agent for flushing magnets but found that when some of the magnets were taken apart, some degradation was found, perhaps due to this chemical. Some test results indicated corrosion rates on copper of one mil/hr (on the inner diameter) using a 100% solution of this agent. Additionally, there were indications of induced stress-corrosion cracking in stainless steels. Pbar tried using citric acid for flushing after learning of the Navy cleaning method and that other industries used citric acid solutions, but found that it was not very effective. Additionally, acid cleaning has been found to change the morphology of the oxide surface and de-passivates it. After cleaning, the surface has copper oxide nodules that do not adhere very well to the surface.

Since 1997, flushing has consisted of backflushing with water using a filtering skid with a turbidimeter installed that indicates when a sector is sufficiently flushed and filtered. A turbidimeter is basically a dual-beam scattered light photometer which indicates the average amount of particulate matter in parts per million by using a focused light beam. It includes the contribution of particles below two μm but does not provide information on the distribution of the particles.

Full-Flow Filtration System

The full-flow filtration system has been recently commissioned. The system consists of two parallel filter housings, with a rated total flow capacity of 2500 gpm at 300 psi, piping to the LCW supply header and associated instrumentation.

Each housing can hold 18 filters, either bag or cartridge. The minimum efficiency of the filter bags is 90% at one micron. Bypass lines around the housings were installed to permit normal operation of the accelerator complex even while changing out the filters. Differential pressure transducers with remote readout capability were installed across the inlet and outlet of each housing. They provide early warning for when the filter media need to be replaced. Previously, the main filtration system consisted of side-stream filters located in the copper headers down in the tunnel.

The ability of the housings to accommodate ultra-fine filters is based on the findings that the median-sized copper oxide particles are about 0.5 micron and that the majority of the particles are smaller than five microns. The side-stream filter housings can only accommodate five micron and up string-wound filters which have about 85% efficiency.

Experience to date with this filtration system indicates very little trapping of particulates after initial commissioning based on virtually no change in the differential pressures.

DISCUSSION

The Pbar magnet plugging phenomenon is a generic problem of systems based on copper cooling coils using low-conductivity water chemistry. The problems in the system were worsened by the lack of any type of filtration until the last few years. Additionally, micro-filtration has not been implemented until the last year.

Recommendations for optimum operating water parameters have been based on field experience. An adequate monitoring of the cooling water circuit together with a safe cleaning method is hoped to contribute significantly to more reliability. This will be determined during the next normal operation of Pbar during Run II.

Although design changes of the magnets which could include replacing the short radius elbows with long radius elbows or increasing the size of elbows could be implemented, cost and time constraints have prevented this option from being pursued on currently installed components. However, as these components are replaced, improved design features, such as larger elbows, have been incorporated.

Additionally, due to time limitations, a detailed study of the chemistry of the system could not be undertaken.

CONCLUSIONS

- The dissolved oxygen concentration is now routinely on the order of 15 parts per billion. This is partially due to the installation of an oxygen-removal system. Prior to the oxygen removal system, oxygen levels were about 3000 ppb. This prevents the production of additional copper oxide in the system.
- Regular closed-loop filter/flushing of the copper headers and magnets and stainless steel header is done during periods when the accelerator is not running. This helps to remove the copper oxide that may already build up.
- Installation of a full-flow filtration system designed to remove any CuO produced by the trace amounts of dissolved oxygen in the LCW system has recently occurred. This system is particularly necessary if any leaks occur which will introduce large amounts of oxygen, and in turn causing the production of copper oxide to drastically increase.
- The Pbar LCW system has operated virtually trouble-free in the past 15 months of operation. This success can be attributed to the system enhancements outlined above.

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